ESTONIAN UNIVERSITY OF LIFE SCIENCES

Institute of technology

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A UV-VISIBLE ABSORPTION SPECTROSCOPY ANALYSIS OF HAFNIUM DIOXIDE AND CARBON NANOTUBES BASED NANOHYBRID MATERIAL FOR SOLAR CELL APPLICATIONS

PÄIKESEELEMENTIDE HÜBRIIDNANOMATERJALIDE UV JA NÄHTAVA VALGUSE NEELDUMISE ANALÜÜS - HAFNIUM DIOKTSIID JA SÜSINIKNANOTORUD

Bachelor thesis

Energy Application Engineering

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Co-supervisors: Prof. Erwan Yann Rauwel,

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Selle bakalaureusetöö eesmärk oli läbi viia spektroskoopiline analüüs nanohübriidmaterjalile koosnevast Hafnium dioktsiidist (HfO_2) ja süsiniknanotorudest (CNT). Uuriti neeldumise lainepikkusi ultraviolett (UV) ja nähtava valguse ergastuse puhul. Eelnevates uuringutes on tuvastatud, et nanohübriid koosnevast CNT'st ja kuupstruktuuriga HfO_2 nanoosakestest tekitab fotovoolu tugeva valgustuse puhul UV ja nähtava valguse puhul. Selles töös uuritakse nanohübriidi koosnevast monokliinilisest HfO_2-st ja CNT-st. Lõputöö üheks ülesandeks oli uurida kuidas mõjub HfO_2/CNT vahekorra muutmine materjali optilistele omadustele. Eesmärgi saavutamiseks segati kokku kolm nanohübriidsegu, mis sisaldasid 5 mg HfO_2-d ja 1, 2, 5% CNT-d kogukaalust, ning mõõdeti segude valgusneelduvust erinevate lainepikkuste puhul kasutades spektrofotomeetrit. Analüüsi tulemusena selgus, et HfO_2-CNT nanohübriid on paremate optiliste omadustega võrreldes puhta HfO_2 või CNT-ga. HfO_2 nanoosakeste puhul märgati neelduvuse tipplainepikkuseid 230 nm ja 265 nm juures. Tipp 230nm juures on seotud elektronide liikumisega HfO_2 aatomite valentstsoonist juhtivustsooni, ületades nende vahe. Tipp 265 nm juures iseloomustab molekulaarseid struktuurisi defekte ja elektronide liikumist pindmistele alamelektronkihtidele. Segades kokku HfO_2 ja CNT täheldati uue neeldumistipu ilmumist lainepikkusel 276 nm juures, mis vastab pindmisele vastasmõjule HfO_2 defektseisundite ja CNT π-plasmoni vahel. Tõstes CNT sisaldust, muutusid

pindmised defektseisundid passiivseteks ning neelduvus 276 nm juures langes. Parima neeldumisega osutus nanohübriid, mis sisaldas 1% CNT-d segu kogukaalust.

Märksõnad: CNT, HfO_2, Neelduvus, spektroskoopiline analüüs, nanohübriid

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Abstract of Bachelor's Thesis

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4.17. Energetic Research

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The objective of this thesis was to perform an absorption spectroscopy analysis on a nanohybrid composite of Hafnium dioxide (HfO_2) and carbon nanotube (CNT). The absorption wavelengths were studied under excitations ranging from the Ultraviolet (UV) to the visible spectrum. In a previous research, it was demonstrated that the HfO_2-CNT nanohybrid containing cubic HfO_2 produces a photocurrent when illuminated with UV and visible light (200-700nm). The current study's key aim was to study the HfO_2-CNT nanohybrid containing monoclinic HfO_2. One of the goals was to study the absorption behavior when the concentration of CNT was varied in the nanocomposite. Three samples containing 1, 2, and 5 wt.% of CNT were prepared and studied using a spectrophotometer. The spectroscopic study revealed that the new nanohybrid has enhanced optical properties as compared to pure HfO_2. For the HfO_2 nanoparticles alone absorption at 230 nm and 265 nm was observed, 230nm corresponding to the fundamental gap of HfO_2 and 265 nm corresponding to defect states of HfO_2. However, when CNT was added, a new absorption peak at 276 nm was observed, corresponding to the surface interactions between HfO_2 defect states and π-plasmon of CNT. The results suggest that when CNT is added, the defect states become passivated and absorption at 276 nm drops.

Keywords: CNT, HfO_2, UV-Vis absorption spectroscopy, hybrid nanocomposite, surface defects

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ACRONYMS AND ABBREVIATIONS

AU	–	Arbitrary units
c	–	Molar concentration M
°C	–	Degrees of Celsius
CB	–	Conduction band
CNT	–	Carbon nanotubes
E	–	Photon energy eV
E_g	–	Band-gap energy eV
EMÜ	–	Eesti Maaülikool, Estonian University of Life Sciences
eV	–	Electronvolt
HfO_2	–	Hafnium dioxide
HfO_2-CNT	–	Hafnium dioxide - carbon nanotube nanohybrid
I	–	Intensity of light cd
l	–	Length cm
MWCNT	–	Multi-walled carbon nanotubes
nm	–	Nanometer
NM	–	Nanomaterial
PV	–	Photovoltaic
P/N junction	–	Interface between p-type and n-type semiconductor materials
QD	–	Quantum dots
SEM	–	Scanning electron microscopy
STEM	–	Scanning transmission electron microscopy
SWCNT	–	Singe-walled carbon nanotubes
T	–	Transmittance %
TEM	–	Transmission electron microscopy
UV	–	Ultraviolet
UV-Vis, UV/Vis	–	Ultraviolet and visible light spectrophotometry
VB	–	Valence band
wt.%	–	weight percentage
ε	–	absorptivity $M^{-1}\cdot cm^{-1}$
λ	–	Wavelength nm

INTRODUCTION

During the past few decades, there has been immense progress in the development of renewable energy sources due to the increasing global energy demand and withering fossil-fuel based energy resources. One of the leading drivers of this progress is the application of new nanomaterials which exhibit superior properties to their bulk counterparts and thereby improving the efficiency of power generation. Nanotechnology has been used in the renewable energy sectors for different applications. For example, nanomembranes have been used in generating hydropower by harnessing osmotic energy [1], anti-reflection coatings made of SiN are used on solar-panels [2] and ultra-light and strong nanocomposites with Al_2O_3 are being used in constructing wind turbine blades [3]. Researchers across the world are making efforts to discover and study new nanomaterials that could play a key role in solving many pressing energy related problems.

This thesis covers a brief study on the absorption behavior of laboratory synthesized nanomaterials and their applications in improving the efficiency of solar cells. In particular, we have studied a novel HfO_2-CNT based hybrid nanomaterial, that is capable of absorbing a wide range of electromagnetic radiation in comparison with the traditionally used materials. The prerequisite of a solar cell is its capability to absorb over a large spectrum, which in turn increases its quantum efficiency. The addition of carbon nanotubes (CNT) in the nanocomposite, further helps in improving the visible light absorption of the hybrid material while as HfO_2 absorbs in the far UV.

The thesis is divided into two parts. The first part covers the literature overview of nanomaterials, HfO_2, CNT and their use in PV applications. The theory of band gaps and UV-Vis absorption spectroscopy is also explained. The second part describes the materials, methodology, experiment results and analysis. The referencing style used in this thesis is that of IEEE, Institute of Electrical and Electronics Engineers.

Nanotechnology is defined as the technology of materials at the nanoscale i.e. the engineering of matter with at least one dimension sized from 1 to 100 nanometers [4]. Nanomaterial's small size implies a very high surface-to-volume ratio and therefore, they exhibit different properties than their bulk-form counterparts. Moreover, combining these nanomaterials into hybrids can introduce entirely novel properties, as explained in this work.

The nanomaterials studied in this thesis are HfO_2 (Hafnium Dioxide), CNT and their combination HfO_2-CNTnanohybrids. CNT are rolled up layers of graphene with their cylindrical diameter smaller than 100nm. They are one of the most studied nanomaterials and have been used in a variety of applications because they offer exceptional properties such as highest tensile strength of all known materials [5], remarkable thermal conductivity and the ability to show metallic or semiconducting behavior depending on their structure. HfO_2 is also a relatively known and highly studied dielectric material. It has been recognized as a vital material in the field of microelectronics thanks to its high dielectric constant. Its first use in semiconductor industry was in 2007 when Intel mixed SiO_2 with HfO_2 as gate insulator in field-effect transistors [6].

1. LITERATURE OVERVIEW

1.1. Nanomaterials

Nanomaterials can be classified in different groups based on their dimensions. Nanosheets, like thin films are materials which have one dimension in the nanometers. If two dimensions are in nanoscale it is a nanotube, for example CNT and if all dimensions are in nanometers it is considered a nanoparticle.

Nanoparticles are not visible through common optical microscopes since the Abbes's diffraction barrier limits the shortest wavelength of visible light to about 200 nm [7]. Instead, they are studied using transmission electron microscopes (TEM), scanning electron microscopes (SEM) and scanning transmission electron microscopes (STEM). [8]

Techniques for synthesizing nanomaterials can be divided into two distinct approaches: top-down and bottom-up, as seen in Fig. 1. The top-down methods involve physically breaking down a bulk material into smaller nanoscale particles and the bottom-up methods combine the atoms and molecules of a material into nanoparticles.

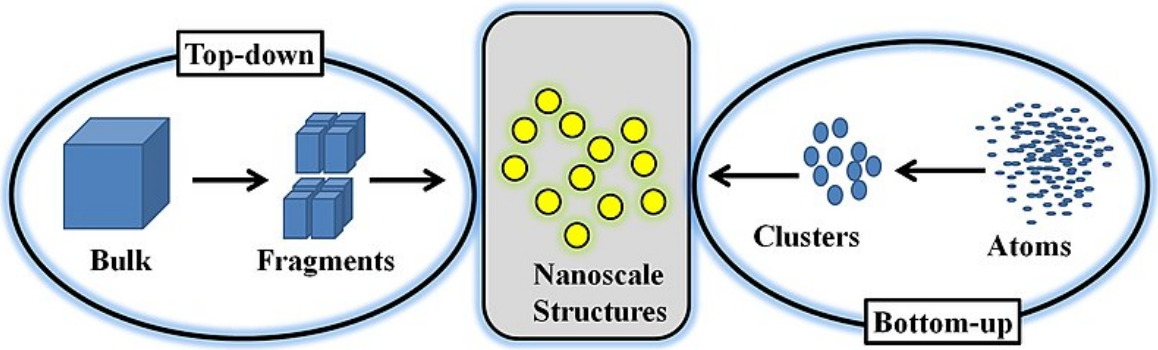

Figure 1. Top-down and bottom-up approaches for synthesizing nanoparticles. [9]

Combining multiple nanomaterials into a nanohybrid is called hybridization and entails the atomic bonding of organic and inorganic materials at the nanometer scale, by noncovalent bonds or covalent bonds. The resulting material will exhibit properties of all substances it contains and can additionally introduce completely novel properties due to synergistic effects between the different components. The method of synthesis also influences the size, shape and properties of nanoparticles.

1.1.1. Hafnium dioxide, HfO_2

Hafnium dioxide or Hafnia with a formula of HfO_2 is a dielectric compound. The name Hafnium is derived from the Latin name for Copenhagen (Hafnia), where it was discovered in 1923 by George Charles de Hevesy and Dirk Coster. Hafnia is a dielectric insulator with a wide band gap of 5.3 ~ 5.9 eV [10], but if it is synthesized in nanoparticles, its band gap can be lower from its in-bulk counterpart. In bulk form Hafnium dioxide is optically inactive, but in nanosize it exhibits photoluminescent properties, due to the increased surface-volume ratio and the presence of surface defects.

Hafnium dioxide has a variety of technologically appealing properties, including a high melting point (2758 °C) and a high dielectric constant (κ= 18-70) depending on its structure [11]. Since new insulating materials with a high dielectric constant are being researched to replace SiO_2 as a gate dielectric, it plays an important role in the continuous downscaling of integrated circuits [6]. Other applications include optical coatings, resistive-switching memories and exotic thermocouples [12], [13]. Hafnium dioxide is considered to be a non-toxic compound and poses no hazard to the human body [14].

Depending on synthetizing conditions, HfO_2 can exist in five different polymorphic structures: monoclinic, tetragonal, cubic, orthorhombic I, orthorhombic II. The most stable states are monoclinic and cubic structures, illustrated in Fig.2. Additionally, cubic and monoclinic HfO_2 nanoparticles are photoluminescent. Depending on the type of structure, the band gap of HfO_2 can vary. Cubic HfO_2 nanoparticles with a diameter of approximately 2.6 nm were studied and a band gap of 4.7eV was noted [15].

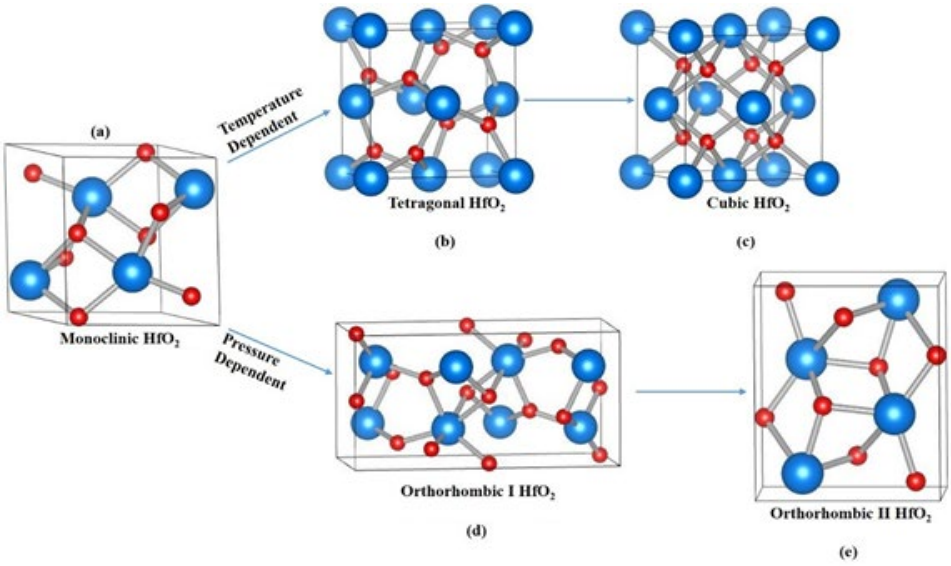

Figure 2. Unit cells of HfO_2 structures (a) monoclinic, (b) tetragonal, (c) cubic, (d) orthorhombic I, orthorhombic II [16].

HfO_2 nanoparticles have been chosen for this thesis because of their optical properties and high potential in photovoltaic cells applications[10][14]. In particular, HfO_2 monoclinic nanoparticles were more particularly studied because most of the studies have been performed on cubic nanoparticles. In the experiments conducted in this study, the monoclinic HfO_2 nanoparticles were not previously studied.

1.1.2. Carbon nanotubes, CNT

Carbon nanotubes were first discovered and described by Sumia Iijima in 1991 and they have been extensively studied to further understand them since then [17]. CNTs have interesting mechanical, electrical, chemical properties and have been used in many different applications. Due to their low toxicity they are used in biomedicine, for example in drug delivery to cells and organs [18]. However, their possible toxicity is still under investigation. CNT exhibit unique optical properties such as sharp absorption peaks, high photoluminescence and very good selectivity in the wavelength of emission, which is why they have been used in photodetectors [19] and LED's [20].

Carbon nanotubes are sheets of one atom thick graphene rolled into tubes. Depending on the number of wall layers there are single-walled carbon nanotubes or multi-walled carbon

nanotubes. The distinction of direction in which graphene sheets are rolled into tubes is called chirality. Band structure calculations predict that chiral CNTs are either semi-conducting or metallic depending on their diameter and helical angle; therefore, the CNT is a candidate for novel electronic devices. In this bachelor thesis MWCNTs are used because they are good electrical conductors [21]. The atomic structure models of carbon nanotubes are shown in Figure 3.

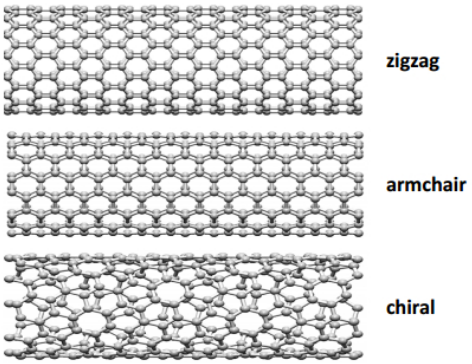

Figure 3. Typical atomic structure models of a CNT.

CNTs are also used as substrates when creating nanohybrids by allowing other nanomaterials to latch on to the defects located on the surface of CNTs. Since there are little defects on a freshly synthesized carbon nanotube, these defects have to be created by a process known as functionalization. One way to functionalize CNTs is through ultrasonication, where the sample is being submerged in liquid and stirred using ultrasonic sound waves.

1.1.3. CNT and HfO_2 nanohybrid

In 2015, Mr. Martin Salumaa studied in his master thesis the functionalization of CNT by ultrasonication and created CNT- HfO_2 nanohybrids. In that study he used cubic phase HfO_2. His goal was to study how the sonication time affects the CNT and to test the resulting nanohybrids for photocurrent generation. The study revealed an improved anchoring of HfO_2 particles for samples which were sonicated for 30 minutes and longer. A maximum theoretical surface coverage of 19.1% was calculated. Electrical measurements demonstrated good electrical conductivity of the nanomaterial and confirmed photocurrent under UV illumination [22].

Mr. Martin Salumaa's findings were taken further by Mr. Andres Aasna in his Master's thesis in 2016, where he tested CNT-HfO_2 and CNT-HfO_2-ZnO nanohybrids. His study reproduced and confirmed the photo-response of CNT- HfO_2 under UV and visible light excitation. Additionally, it revealed that adding ZnO into the compound did not improve the photocurrent properties of the hybrid nanomaterial [23].

The unique photocurrent generation properties of CNT and CNT-HfO_2 nanohybrids under UV and visible light excitations were further studied and again confirmed in articles published in 2016 and 2019 by Rauwel et. al [15], [24]. According to all present studies, CNT-HfO_2 appears to be a very promising material for photovoltaic energy harvesting applications.

This bachelor thesis carries on the previous research and focuses on spectroscopic efficiency analysis of the HfO_2-CNT nanocomposite, by varying the concentration ratio of CNT and monoclinic HfO_2 nanoparticles. Nanohybrids of the monoclinic HfO_2 with CNT have not been studied before.

1.2. Band gaps and energy harvest

The working principle of classic photovoltaic cells is based on semiconductors and a p-n junction, by harvesting the energy carried by a photon and converting it into electricity. The energy is only transferred to the conduction band, if the photon carries enough energy to excite the materials' electron high enough to make the electron jump over the band gap, also known as the energy gap. The term "band gap" refers to the energy difference between the top of the valence band and the bottom of conduction band. That energy is measured in electronvolt (eV). If sufficiently excited with a quantum of energy equal or greater to the bandgap, then the electron is able to jump from valence band to the conduction band. Once the electron crosses over to the conduction band the material starts conducting electricity. Materials have different band gap, they require different amount of energy for their electrons

to cross the band gap. For example, the band gap of insulators is high (> 4eV) and lower for semiconductors (<4eV) as seen in Figure 4.

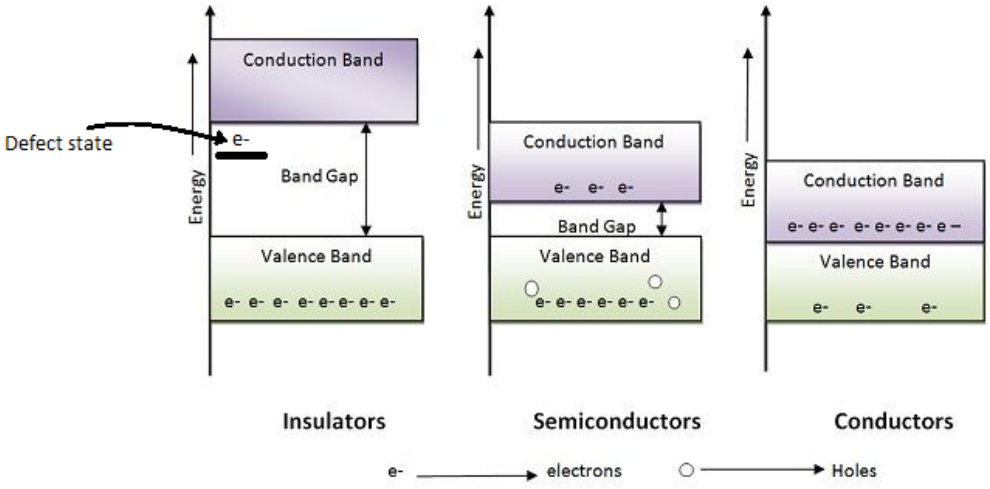

Figure 4. Diagram for band gaps of insulators, semiconductors and conductors [25].

The band gap energy level is important because it determines the portion of the solar spectrum a solar cell is able to absorb. A big part of the solar radiation emitted by the sun and reaching the Earth consists of wavelengths with energies greater than the band gap of silicon, the most common semiconductor material used in solar cells. This means that for silicon the energy, which is left over the energy gap will be absorbed by the solar cell, but instead of carrying electrons and generating usable electrical energy, it will be converted into heat and therefore wasted in this context. By using materials with other band gaps it is possible to harvest a different, wider spectrum of the electromagnetic radiation and therefore increase the quantum efficiency of the solar cell.

In a semiconductor, photons with at least energy equivalent to the band gap of the materials are able to excite electrons capable of crossing the band gap and generate a current. However, some photons with energies below the band-gap energies are still able to excite electrons to higher-energy states, as shown in Figure 3. Thereby it is possible to generate photocurrent even in dielectrics, by using a charge carrier material with metallic properties like CNT to capture electrons in the surface states. Using this method, a solar cell without a p/n junction is created. This was the mechanism used to generate photocurrent in CNT-HfO_2 nanohybrids

in the previously discussed studies [15], [24] and it has proved its high potential for photovoltaic energy harvesting solutions. In this thesis, the spectroscopic analysis of CNT-HfO_2 is carried out for better understanding of the material and is intended for future use in below the band gap photocurrent generation.

1.3. Limits to solar cell energy conversion efficiency

In 1961 William Shockley and Hans-Joachim Queisser calculated a radiative efficiency limit, which is the maximum theoretical energy conversion efficiency of a solar cell, illustrated in Figure 5. It is the percentage of power converted from the sunlight to electrical energy using a single p-n junction to collect power from the cell where the only loss is from radiative recombination.

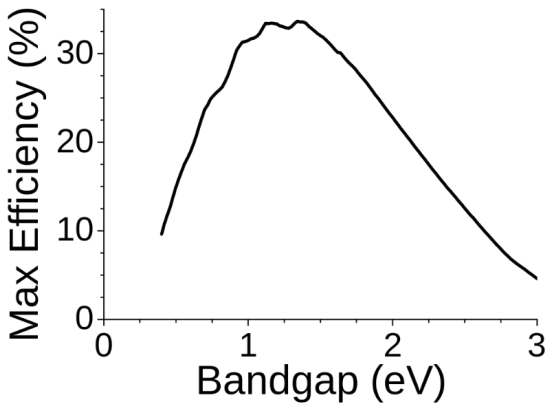

Figure 5. The Shockley–Queisser limit for the efficiency of a solar cell [26].

The SQ limit, first calculated to be 30% at 1.1 eV and later improved to 33.7% for a bandgap of 1.34 eV, means that of all the power contained in sunlight (around 1000 W/m^2) falling on an ideal solar cell, only 33.7% could ever be turned into electricity (337 W/m^2). For the most common solar cell material silicon it is around 32%. In reality, commercially available solar panel conversion efficiency peaks at around 24%. This is because of all the light from the sun that reaches the earth, around a tenth of it is reflected back into the atmosphere.

But the Shockley-Queisser limit of 33,7% only applies for a solar cell under the following critical assumptions [27]:

- Solar cell uses only one semiconductor material
- Solar cell uses only one P/N junction
- Solar cell is powered by non-concentrated sunlight - a “one sun” source, air mass coefficient of 1.5 (AM1.5) - corresponds to solar zenith angle of z=48.2°.
- Energy from photons greater than the band gap is converted into heat

And what do the 67% of the energy losses account for?

- 47% of the energy gets converted into heat
- 18% of the photons pass through the cell
- 2% is lost from local recombination from newly created holes and electrons

In Figure 6. the complete spectrum of the electromagnetic radiation with the solar and visible light spectrum is shown. The short, X-rays have the highest energy and the long radio waves have the lowest amount of energy. The solar spectrum ranges from 165 to 3000 nm and it includes ultra-violet, visible and infrared light. The UV light has the wavelength of 100-400 nm and travels with energies ranging from 12.4 - 3.1 eV. Visible light has the wavelength of 400 - 700 nm photon energy of 3.3 eV - 1.7 eV. Infrared light has the wavelength of 700 nm - 1 mm and photon energy of 1.7 eV - 1.24 eV.

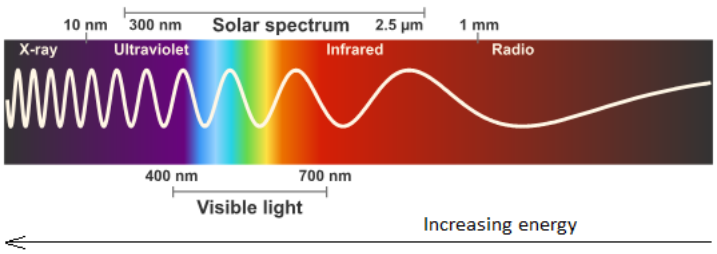

Figure 6. Illustration for the complete electromagnetic radiation spectrum with solar spectrum and visible light wavelengths [28].

In Figure 7, the mustard colored area is a representation of Shockley-Queisser Limit applied to silicon as they calculated it in 1961.

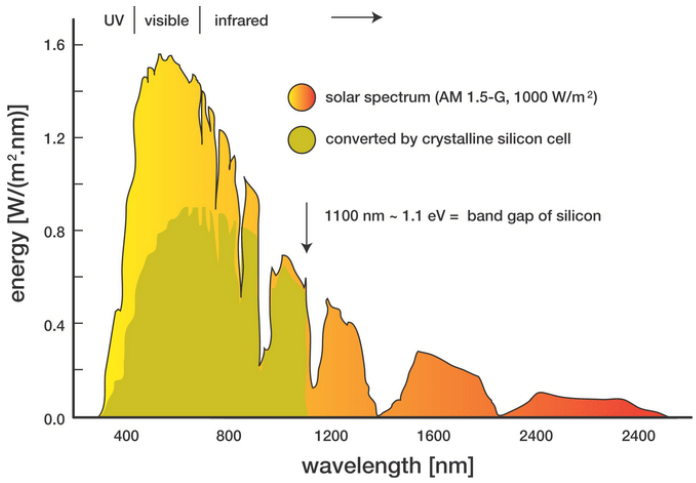

Figure 7. Solar irradiance energy and wavelength spectrum, wavelengths absorbed by Si cells [2].

The infrared light with the wavelengths of 2500-1200 nm (orange area) does not have enough amount of energy to be absorbed and a big part of the visible and UV light (yellow area) has too high level of energy. The visible and UV light is absorbed and generates electricity, but a lot of energy is still lost. This is because photons with band gap energies higher than that of Si (>1.1 eV) generate a free electron and a hole, but their extra energy gets dissipated as heat.

1.4. Using nanotechnology in PV to increase efficiency

It is possible to obtain better efficiencies than the SQ limit predicts and the strategies to do that involve addressing previously mentioned losses by finding a work-around to one or more of the critical assumptions listed above (and shown again below). The use and combining of nanotechnologies opens the door to many of these workarounds.

- "Solar cell uses only one semiconductor material"

To overcome this limitation, it's possible to use more than one semiconductor in a single cell or to manipulate a material which is not a semiconductor overall. Below the band-gap photocurrent generation in CNT-HfO_2 nanohybrids falls under the second category, as there a dielectric is used instead of a semiconductor [15], [24].

- “Solar cell uses only one p-n junction“

In this case again, below the band-gap photocurrent generation is a solution since it does not use a p-n junction [15], [24]. Also, the use of more than one junction in a single cell - tandem cells can be the solution. Thin film tandem solar cells enable to absorb a larger fraction of the solar spectrum [29]. Tunnel diodes have been used in tandem cells as nano-antennas and electromagnetic collectors to draw in charges [30].

- “Solar cell is powered by non-concentrated sunlight - a “one sun” source, AM1.5”

There are multiple ways to overcome this limitation. For example, it is possible to use lenses to concentrate sunlight [29] or to use an external electric field to funnel and concentrate charges [31].

- “Energy from photons greater than the band gap is converted into heat”

Using quantum dots to absorb excess photon energy or combining the solar cell with a heat based energy harvesting technology is the workaround for this assumption. The use of extremely small nanocrystals or semiconductor quantum dots (QD) allows for improved light absorption of solar cells and thereby has improved their efficiency [32].

In particular, Hafnium-based compounds and carbon nanotubes have previously already been used in solar energy applications. For example, thin HfO_2 antireflection coatings are used to increase the amount of light that enters a PV cell by reducing surface reflections, since more than 30% of the light that strikes a coated silicon wafer is reflected [33], [34]. Inverse charge-funneling with an external electric field by using a few-nanometer thin sheet of HfS_2 has shown to enable to bring the efficiency up to 60% in laboratory settings [31]. Dye-sensitized solar cells use nanometer sized Titanium dioxide particles as dye molecules and carbon nanotubes as charge carriers within those dyes [35], [36].

1.5. UV-Vis absorption Spectroscopy

Absorption spectroscopy or reflectance spectroscopy in the ultraviolet and neighboring visible regions of the electromagnetic spectrum is referred to as UV-Vis spectroscopy. It is

possible to measure the absorption of radiation of all wavelengths, but we are focusing on the ultra-violet spectrum range of 200-400 nm and the visible light spectrum range of 400-700 nm, Atoms and molecules undergo electronic transitions in this portion of the spectrum. The color of the chemicals involved is specifically affected by their absorption or reflectance in the visual spectrum. By using a spectrophotometer and measuring the fraction of light transmitted through the studied material, we are able to determine the amount of absorbed energy. The increase in transmission implies decreasing absorption.

Absorbance can be related with transmittance by the relation as follows [37]:

$$A = log_{10} \frac{I}{I_0} = -log_{10} T \tag{1.1}$$

where A is the absorbance of light AU;

T - transmittance ratio of two intensities;

I_0 - intensity of light before it passes through the sample cd;

I - intensity of light after it passes through the sample cd;

Absorbance has a logarithmic relationship to the transmittance; with an absorbance of 1 corresponding to 10% transmittance and an absorbance of 0 corresponding to a transmittance of 100%. Absorbance is a dimensionless quantity and should, therefore, be unitless or marked as arbitrary units (AU) for clarification.

Absorption can also be determined using the Beer-Lambert law, which states that there is a linear relationship between the solutions absorbance and the concentration, molar absorption coefficient and the path length. Beer-Lambert law is mostly used to determine the concentration of chemical solutions.

The equation and explanation of it is shown below [38].

$$A = \varepsilon l c \tag{1.2}$$

where A is the absorbance of light AU;

ε - Absorptivity or the molar attenuation coefficient $m^{-1} \cdot cm^{-1}$;

l - Length of the beam in the absorbing medium cm;

c - Molar concentration of the absorbing species M;

The instrument used to measure absorption in the ultraviolet-visible spectrum is called a UV-Vis spectrophotometer. It compares the intensity of light after it passes through a sample (I) with that of light before it passes through the sample (I_0).

Below is an illustration depicting the components of a typical spectrophotometer and the path of the light beam, seen in Figure 8.

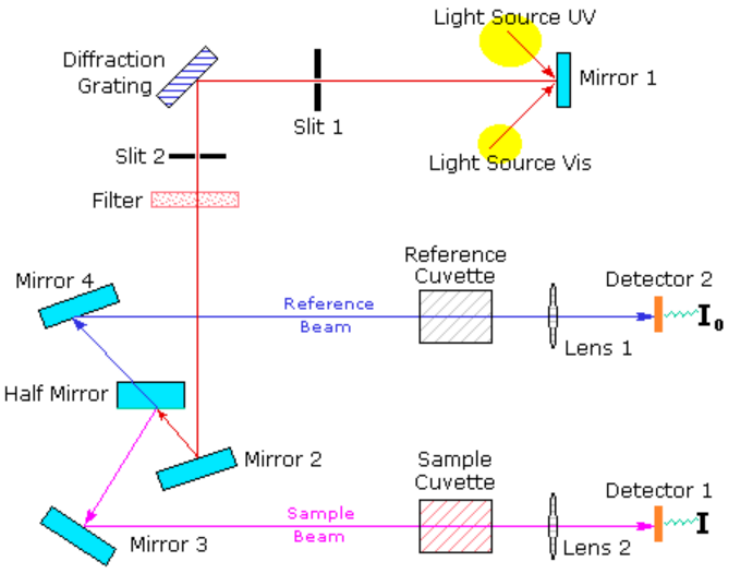

Figure 8. Illustration of basic components and construction of a typical spectrophotometer [39].

A beam is created using a halogen lamp for the light in the visible range and a deuterium lamp for light in the UV range. The beam goes through a slit and the diffraction grating separating the different wavelengths. The separated light goes through the second slit and the filter after which the beam is halved into a reference beam and a sample beam using a halving mirror. Finally, the two light beams go through the reference cuvette and the sample cuvette. The light is concentrated through lenses and passed onto the detectors to measure the light intensity and compare the two results I_0 and I

2. AIMS AND OBJECTIVES

The main objective of this thesis is to conduct spectroscopic analysis on the HfO_2-CNT nanohybrid material. The aim of this work is to determine the exact wavelengths absorbed by the HfO_2-CNT nanohybrid compound and to study the effect of varying concentration of CNT in the nanocomposite on the properties of the new nanohybrid. A suggestion for the most effective ratio range will be made for future use of HfO_2-CNT in this research.

Previous research has shown that nanohybrids containing CNT and cubic HfO_2 have a high potential to be used in photovoltaic applications by confirming that this compound has a high photo-response and absorbs UV and visible spectrum of light. In this thesis, HfO_2-CNT nanohybrids with HfO_2 nanoparticles in the monoclinic form are studied as this has not been done before. Having a deeper understanding of monoclinic HfO_2-CNT nanohybrids optical properties could be helpful in future investigations.

We have selected the samples that contain 5 mg of HfO_2 and 1, 2, 5 wt.% of CNT. The spectroscopic analysis was conducted in the range of 200-700 nm. The documentation and the results of these experiments are presented in practical work section.

3. MATERIALS

3.1. Equipment

The main instrument used in experiments was the UV-VIS Spectrophotometer MACHERY NAGEL NANOCOLOR UV/VIS II and is show in Figure 9. It is capable of measuring absorption with the accuracy of ±1nm and a resolution of 0.1nm. The suitable wavelength range for measurements is 190-1100 nm [40].

Figure 9. MACHERY NAGEL NANOCOLOR UV/VIS II spectrophotometer [40].

The samples were measured using two quartz glass cuvettes with an optical path of 10 mm. One was for reference measurements, and the other was for sample measurements. The samples were stirred and the CNT was functionalized using ultrasonic waves in a "SONICA" ultrasonication tank.

Before spectroscopic analysis, the alcohol was dried out of the samples in an oven "Memmert". Three "Eppendorf" research pipettes L17747E for 0.5-5 mL, M19572H for 20-200 mL, and J54259H for 100-1000 mL, were used to accurately measure the amount of CNTs in Ethanol. The HfO_2 nanoparticles used in the samples were weighed using a precision cube scale KERN ABJ-NM. Its measurement readability (reading uncertainty) is

0.1 mg, weighing range is from 0.01g to 220g. The samples were stored in glass beakers and plastic falcon tubes.

3.2. Chemicals

Since the CNT were dispersed in ethanol, ethanol was also used as a solvent to combine the CNTs and HfO_2. However, Isopropanol was used as a solvent to hold the nanohybrid compound during spectroscopic analysis in the spectrophotometer.

The monoclininic HfO_2 particles with an average diameter of ~2.6 nm used in the experiments were synthesized by Rauwel et al. using the non-aqueous sol-gel process [41]. The sol-gel method is a bottom up synthesis approach and a wet chemical procedure that is mostly used to make high-purity and homogeneous metal oxide nanoparticles and ceramic powders.

The CNTs used in the experiments were multi walled carbon nanotubes. These NANOCYL NC7000 MWCNTs with an average length of 1.5 nm and diameter of 10 μm, were purchased beforehand.

4. EXPERIMENTATION

4.1. Preparation of solutions

5 samples were studied in this thesis. Pure HfO_2, pure CNT and three mixtures of both nanomaterials at different concentrations. In the mixture samples, the amount of HfO_2 was 5 mg and the weight% of CNT was 1%, 2% and 5%.

The nanohybrid samples were prepared in the following way:

1) Calculating the amount of CNT and HfO_2 to get the right weight percent in the mixture samples.
2) Weighing CNT and HfO_2 and combining them together in ethanol.
3) Submerging the solution in ultrasonicator for 5 minutes to functionalize CNT and to attach HfO_2 onto CNT.
4) Drying out the ethanol from the CNT and HfO_2 nanohybrid by keeping the samples in a laboratory oven at 60°C.

Before work could begin it was necessary to calculate the amounts of CNT and HfO_2 to mix together in order to achieve correct proportions and weight%. Every sample needed to contain 5mg of HfO_2 and 1%, 2%, 5% of CNT. At the start of experiments, the CNT was already in the ethanol solution. The concentration ratio of the mixture was 4mg of CNT per 50 ml of Ethanol. which is 12.5 g of Ethanol per 1 mg of CNT.

$$1\ mg\ CNT\ = \frac{50}{4} \equiv 12.5\ ml\ Ethanol.$$

The HfO_2 was in a dry, powdered state. In order to get a mixture containing 1mg of HfO_2 and with CNT 1% of total weight, 0.125 of Ethanol needed to be extracted.

$$100\%\ HfO_2 \equiv\ 1\%\ CNT$$

$$1\ mg\ HfO_2 \equiv\ 0.01\ mg\ CNT$$

$$\text{Since, } 1\ mg\ CNT \equiv 12.5\ ml\ Ethanol.$$
$$\text{Then, } 0.01\ mg\ CNT \equiv 0.125\ ml\ Ethanol$$

Therefore, if we have 5mg of HfO_2, we repeat the same calculation but instead of 1mg of HfO_2 we have 5mg.

$$0.01\ mg\ CNT \equiv 12.5 \cdot 0.01 = 0.125\ mg\ Ethanol$$
$$0.05\ mg\ CNT \equiv 12.5 \cdot 0.05 = 0.625\ mg\ Ethanol$$

For a 1wt.% solution we needed to extract 0.625 mg of Ethanol containing CNT. Next, in order to mix a solution with 2 wt.% and 5% wt.% the previous calculation was repeated replacing 1% of CNT with 2% and 5%. The resulting quantities are shown in Table 2.

Table 1. Resulting solution samples

Serial No.	Weight percent, %	Concentration of HfO2	Concentration of CNT	Concentration of Ethanol
1.	100% CNT	-	5 mg	-
2.	100% HfO_2	5 mg	-	-
3.	1% CNT	5 mg	0.05 mg	0.625 ml
4.	2% CNT	5 mg	0.10 mg	3.125 ml
5.	5% CNT	5 mg	0.25 mg	3.25 ml

The ethanol was dried out of the samples keeping them in the laboratory oven at 60°C for 2 days. Further, the samples were prepared for UV-Vis spectroscopic analysis which is described in the next chapter.

4.2. UV-Visible spectroscopic analysis

Next, the nanohybrid was prepared for the UV-Vis absorption measurements in the spectrophotometer. The nanohybrid samples were diluted in isopropanol. Then, the samples were stirred in the ultrasonication tank to get achieve an even distribution throughout the sample. Quartz cuvettes with an optical path of 10mm were used for the measurements. The sample cuvette was filled with the sample solution and the reference cuvette was filled with pure isopropanol. The sample solutions were measured for absorption of UV-Visible light at 200-700 nm using a spectrophotometer in the normal and high-precision mode. Measurement results were exported with a USB-stick and processed.

4.3. Results and Discussion

12 measurements were made using the spectrophotometer. The data with the highest quality and the least amount of noise was saved and studied further. Below is Table 2. describing peak absorption wavelength values and Figure 10. that shows the graphs drawn in the software Microsoft Excel using the XLS data exported from the spectrophotometer.

Table 2. Peak wavelength measurement values of the samples from the spectrophotometer

Serial No.	Sample	Peak 1	Peak 2
1.	Pure CNT	203	249
2.	Pure HfO_2	230	265
3.	1 wt.% CNT in HfO_2	230	276
4.	2 wt.% CNT in HfO_2	230	276
5.	5 wt.% CNT in HfO_2	230	276

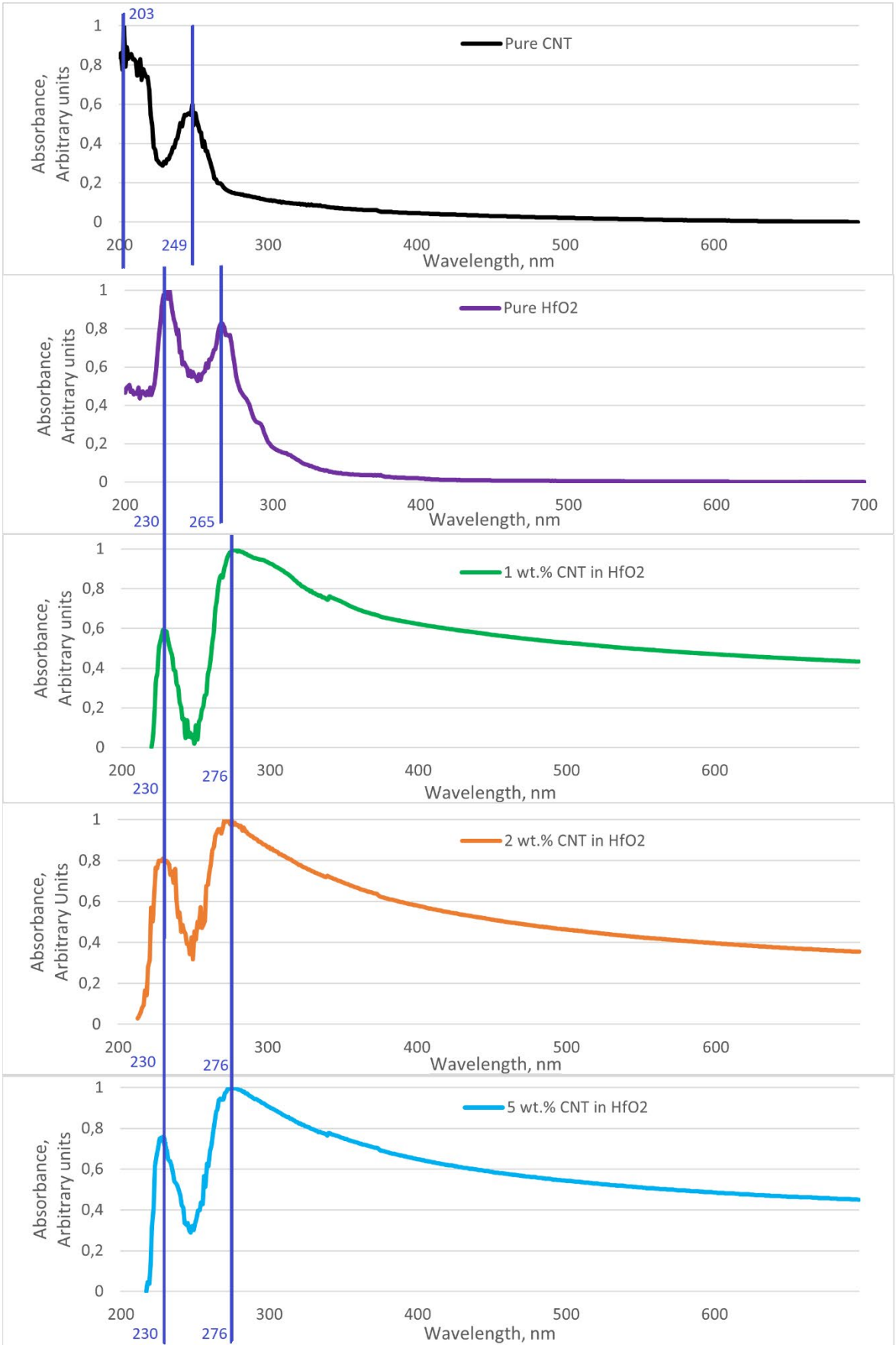

Figure 10. Sample measurement results from UV-Vis. spectrophotometer.

The pure CNT showed two absorption peaks: one at 203 nm and another one at 249 nm. Both of them represent the excitation of the π-plasmon. CNT is a rolled-up layer of graphene and it consists of a layer of carbon atoms packed in a 2D honeycomb lattice with three sp^2 hybridized orbitals oriented in the x-y plane and having a mutual angle of 120° between them and this forms six σ-bonds. CNT also has the unhybridized 2p orbital which is perpendicular to the x-y plane and forms π-bonds. The electrons moving in these orbitals are called the π-electrons and the oscillation of its plasmons is called the π-plasmon. The π-plasmons are able to absorb and carry electrons easily. Since they are perpendicular to the x-y axis of graphene they are located on the surface of CNT and inside, between the layers. The peak at 203 nm is related to the bulk π-plasmon, and the one at 249 nm is due to the surface π-plasmon of CNT.

Pure HfO_2 showed the absorption peaks at two different wavelengths: 230 nm and 265 nm. The first peak in absorption at 230 nm is due to the bandgap of HfO_2, illustrated in Fig 11. as the yellow line between valence band and conduction. The second peak, at 265 nm is related to the surface defects on the HfO_2 molecules creating alternative states that the electron can transition to. The electrons in the valence band are excited to the higher-energy states, which are somewhere between the band gap, illustrated in Fig 10. as electrons at Vo and V_{Hf} levels.

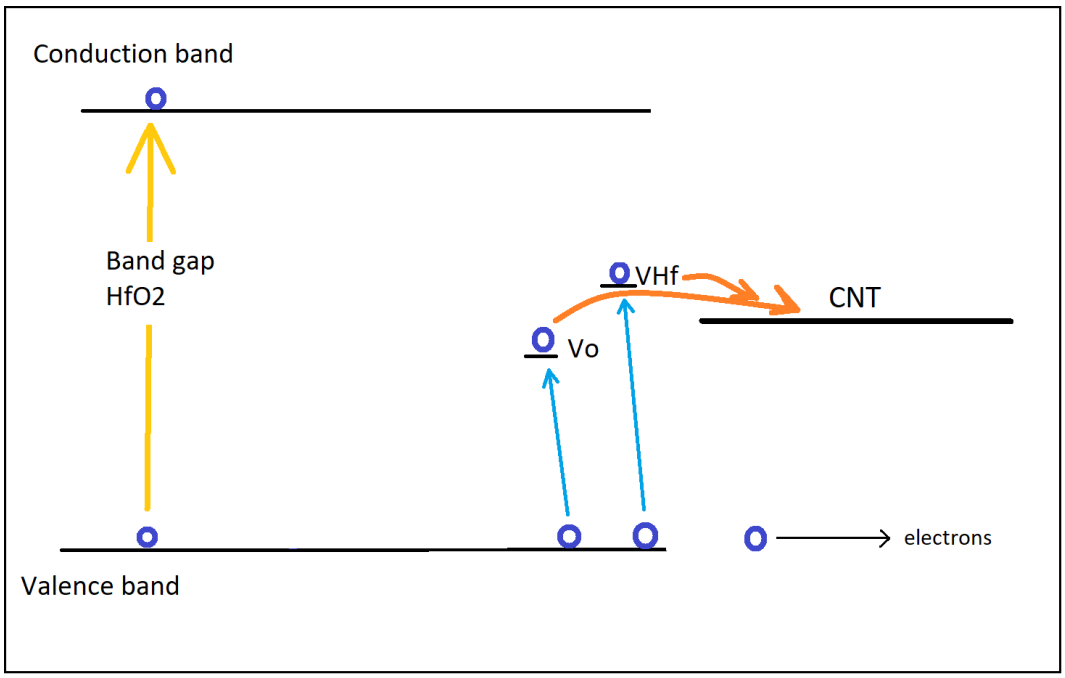

Figure 11. Illustration of electronic transitions in a HfO_2-CNT nanohybrid

Forming a hybrid from these compounds reveals new optical properties, which are different from pure HfO_2 and CNT as the peak absorption wavelengths shift. When we analyze the nanohybrid composite absorption wavelengths we note again two peak values, first at 230 nm and second at around 276nm. The peak at 230 nm is again due to the electronic transitions of HfO_2 from the valence band to the conduction band and creating current. The peak around 276 nm once again represents the effect of surface defects on HfO_2.

All measured nanocomposite samples exhibit a much higher absorption in the >276 nm range, compared to the absorption of wavelengths in pure CNT and HfO_2 related to defects and surface states. In other words, the decline of absorption after the second peak, also known as the offset, is much more gradual in the hybrid samples, compared to the steep drop in the absorption of pure CNT and HfO_2.

On its own, HfO_2 has few surface defects and therefore, a small amount of surface states is present, illustrated in Figure 10 by the ratio of the peaks and the peak being lower than the first. The surface states that do exist are quickly occupied and only by electrons excited by photons of very narrow wavelengths. CNT has metallic properties as its fermi level lies in the range of band gap of HfO_2. Therefore, upon combining CNT and HfO_2 into a nanohybrid, it can be suggested that CNT has the potential to act as a charge carrier as the excited higher energy electrons at defect states, Vo and V_{Hf} could pass over to the CNT and conduct current, illustrated in Fig. 11 as the orange lines moving from Vo and V_{Hf} to the CNT band.

The nanohybrids absorption represented by HfO_2 is more prominent than CNT, because the signature absorption peak of HfO_2 is still clearly visible at 230 nm. However, other peaks at 276 nm are now present, because of the bonds between π-electrons of CNT and electrons at the defect states of HfO_2.

As seen from the results, the amount of CNT in the solution does affect the absorption properties of the hybrid. Upon increasing the amount of CNT in the nanohybrid, the ratio between the absorption peak values changes. Table 3 shows the non-normalized absorption levels at peak absorption wavelengths.

The ratio is expressed as the absorption value of second peak divided by the absorption value of the first peak. The first peak of 230 nm corresponds to the band gap transitions of HfO_2. The second absorption peak at 276 is representing the interactions between CNT and the defect states of HfO_2: the oxygen vacancy Vo and the excited V_{Hf}. The absorption at the second peak is compared to the first, because the amount of HfO_2 is constantly 5 mg in all the samples. The second peak is treated as a variable, because the concentration of CNT in the samples is changing and therefore the number of interactions between CNT and the defect states is also varying.

The comparison of the ratios shown in Table 3 allows us to see which electronic transitions are more prominent in the nanohybrids depending on the amount of CNT in the samples. The absorption peaks of pure HfO_2 are also analyzed for comparison with the hybrids.

Table 3. Proportionality of absorption levels at the two peaks.

Sample	Absorption level, AU		Proportionality, AU
	Peak 1 - 230 nm Band gap transitions	Peak 2 - Defect related transitions	$\frac{Peak\ 2}{Peak\ 1}$
Pure HfO_2	1.007	0.844	0.84
1 wt.% CNT in HfO_2	0.580	0.978	1.67
2 wt.% CNT in HfO_2	1.313	1.444	1.09
5 wt.% CNT in HfO_2	0.715	0.815	1.14

From the ratio of absorption peaks of pure HfO_2 it is clear that the band gap transitions are more prominent, and the defect related transitions are less prominent as the absorption level of peak 2, of wavelengths related to defect transitions is smaller compared to the absorption level of peak 1 - wavelength of 230 nm. The ratio between them is around 0,84.

Once CNT is added into the samples though, the defect related transitions become more prominent, due to the increasing interactions between CNT and HfO_2 as seen from the risen absorption level of the second peak. The sample with 1 wt.% of CNT exhibits the highest level of transitions related to the defect states, the ratio is 1.67.

However, once the concentration of CNT is increased to 2 wt.% the ratio of absorptions drops to 1.09. This drop in absorption is likely occurring due to the passivation of HfO_2

defect states, as the surface of HfO_2 gets saturated with CNT and thereby blocks absorption of photons. When the concentration of CNT is further increased to 5 wt.%, the absorption at the defect peak slightly rises again as compared to band gap peak. This is likely due to the hindrance of the already formed bonds between CNT and HfO_2 defect states which allows for more electronic transitions and thus increasing absorption.

These results indicate a statistically significant difference of the ratio of HfO_2-CNT in the nanohybrid as it determines in the type of absorption and the implied nature of the electronic transitions. The deeper cause and the main factor explaining this dependence on nanomaterial ratio is suggested to be related to the passivation and hinderance of the defect states as more CNT gets anchored on the defects of HfO_2 nanoparticles.

SUMMARY AND CONCLUSION

The main objective of this Bachelor's thesis was to conduct UV-Vis absorption spectroscopy analysis on the HfO_2-CNT nanohybrid material. The goal was to study how the HfO_2-CNT nanohybrid compound behaves under UV and visible light excitation and to investigate the effect of varying the concentration of CNT in the composite on the properties of the nanohybrid.

Three samples of nanohybrid compound were prepared, each containing 5mg of HfO_2 mixed with 1, 2 or 5 wt.% of CNT. First, HfO_2 was mixed with CNT using Ethanol as a solvent, where CNT was contained beforehand. Ultrasonic treatment was used to disperse the CNT and to functionalize them by creating defects in the structure of CNT that promote the anchoring of HfO_2 nanoparticles on the surface of the CNTs. Then, ethanol was dried out of the samples by keeping the samples in an oven at 60°C for 2 days. After that, the dry nanohybrid compound was diluted in isopropanol, and sonicated to prepare a colloidal solution that can be characterized by spectroscopic analysis.

The nanohybrid compound samples along with pure HfO_2 and CNT were studied using a UV-Vis spectrophotometer. The samples were inserted into the spectrophotometer using Quartz cuvettes with a 1cm optical path length and the absorption wavelengths in the range of 200-700 nm was measured.

The spectroscopic analysis revealed that the combined characteristic of HfO_2 and CNT nanohybrid presents different optical adsorption compared to pure HfO_2 or CNT. The analysis of hybrid samples presents two peak absorption wavelengths, first at 230 nm and second at 276 nm, which are different from the ones of HfO_2 or CNT. The first peak is due to the band gap electronic transition of HfO_2. The second peak is related to the molecular structure defects and activation of surface states by combining HfO_2 and CNT.

The analysis revealed that varying the ratio of CNT in the compound affects the absorption as the ratio of absorption changes. Upon increasing the amount of CNT, the absorption related to defect related transitions at peak 2 drops in comparison to band gap transitions of peak 1. This is likely due to the occurring passivation of HfO_2 nanoparticles as the surface of HfO_2 nanoparticles gets saturated with CNT. As the concentration of CNT is increased, also the number of surface states of VHf and Vo bonded with CNT rises. The surface of HfO_2 gets covered with CNT, and subsequently the absorption drops.

The most effective ratio with the highest absorption related to the interaction between CNT and the defect states of HfO_2 was with 1 wt.% of CNT. In all of the samples, the properties of HfO_2 were more dominant, compared to the ones of CNT, according to the peak at 230nm which is the characteristic to HfO_2.

The results presented in this bachelor thesis demonstrate the high potential of using monoclinic HfO_2-CNT nanocomposites in photovoltaic applications as it exhibits good absorption in the UV-visible spectrum range. For example, HfO_2-CNT nanohybrid composite could be used as a single-layer thin film solar cell to harvest below the band gap energy or it can be used in multilayered photovoltaic elements, tandem-cells. This could increase the efficiency of the solar cell.

Further research on the effect of varying the nanomaterial ratios is needed to understand the mechanism that occurs during absorption. Also, testing for photocurrent generation in monoclinic HfO_2-CNT based nanohybrid should be carried out as this thesis only focused on determining the absorption wavelengths that could potentially generate photocurrent. The advantage of researching this material is that HfO_2-based devices are already produced and used in the microelectronic industry, making their introduction into nanosystems easier. Due to already developed technical frameworks, this can speed up the production and introduction of emerging HfO_2-based technologies.

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ÜLDKOKKUVÕTE

PÄIKESEELEMENTIDE HÜBRIIDNANOMATERJALIDE UV JA NÄHTAVA VALGUSE NEELDUMISE ANALÜÜS - HAFNIUM DIOKTSIID JA SÜSINIKNANOTORUD

Käesoleva bakalaureusetöö eesmärk oli läbi viia UV ja nähtava valguse neeldumise analüüs nanohübriidmaterjalidest koosnevast monokliinilisest hafniumdioksiidist (HfO_2) ja süsiniknanotorudest (CNT). Eelnevates uuringutes on tuvastatud, et nanohübriidist koosnevast CNT'st ja kuupstruktuuriga HfO_2 nanoosakestest tekib tugeva ultraviolett ja nähtava valguse 200-700 nm spektri puhul fotovool. Sellest ilmneb vajadus uurida ka monokliinilist HfO_2-d sisaldavat HfO_2-CNT nanohübriidi, et välja selgitada selle potentsiaal energeetikatööstuses kasutamiseks, näiteks päikesepaneelide elementides. Selle töö eesmärkideks oli välja selgitada hübriidmaterjalide valgusneeldumise täpsed tipplainepikkused ning uurida kuidas mõjub HfO_2/CNT vahekorra muutmine materjali optilistele omadustele.

Töö on jaotatud kahte ossa. Esimene pool sisaldab kirjanduse ülevaadet nanomaterjalidest, hafnium dioksiidi nanoosakestest, süsiniknanotorudest ning nende kasutusest päikeseenergeetikas. Kirjeldatakse päikeseenergia tootmise puhul olulisi mehhanisme ning kuidas nanotehnoloogia kasutamine on üks viisidest kuidas tõsta päikeseenergeetika efektiivsust. Samuti selgitatakse UV ja nähtava valguse neeldumise analüüsi protsessi.
Töö teine osa sisaldab kasutatud uurimisseadmete, materjalide kirjeldust ja uurimismetoodikat. Tuuakse välja tehtud arvutused, eksperimentide läbiviimise kord ning tulemused ja analüüs. Antud töös on kasutatud IEEE viitamissüsteemi.

Püstitatud eesmärkide saavutamiseks viidi läbi valguse neeldumise katsed, mille protseduur nägi välja järgmiselt. Segati kokku kolm HfO_2-CNT nanohübriidsegu, millest igaüks sisaldas 5mg HfO_2-d ja 1%, 2%, 5% CNT'd segu kogukaalust. Ainete täpsed kogused ja

vahekorrad on välja toodud tabelis 2. Kahe aine kokku segamisel kasutati lahusena etanooli, kuna CNT'd olid hoiustatud algselt selles. Nanohübriidmaterjali võrdse hajutuse saavutamiseks ning HfO_2 molekulaarseks kinnitumiseks CNT pinnale kasutati ultrahelitöötluse meetodit.

Ultrahelitöötlus tekitab CNT ja HfO_2 struktuuris molekulaarseid defekte/vigasid/tasakaalutusi, mis soodustavad osakeste kinnitumist üksteise külge. Nanohübriidmaterjalist kuivatati välja etanool hoides lahust laboratoorses ahjus 60°C juures 48 tundi. Seejärel lahustati nanohübriid isopropanoolis, sest töös kasutatud mõõteseade oli võimeline aine neelduvust mõõtma ainult destilleeritud vees või isopropanoolis. Lahust töödeldi jälle ultraheliga, et valmistada võrdse hajutusega lahus, mida saab karakteriseerida spektroskoopilise analüüsi teel.

Seejärel uuriti lahuste valgusneelduvust ultra-violetse (UV) ja nähtava valguse spektrofotomeetriga lainepikkuste 200-700 nm piires. Mõõdeti puhast HfO_2'd, puhast CNT'd ja nanohübriidmaterjali lahuseid kolme erineva CNT kontsentratsiooni juures.

Tulemuste analüüsil tulemusena selgus, et HfO_2 ja CNT kombineeritud nanohübriidi omadused on erinevad võrreldes puhta HfO_2 või CNT omadustega. Ilmnes märgatav muutus valgusneelduvuse tipplainepikkustes, mis on välja toodud tabelis 3 ja illustreeritud joonisel 14. Uuel nanohübriidmaterjalil on kaks neelduvuse tipp-lainepikkust. Esimene on 230 nm juures ja teine 276 nm juures, mis on erinevad puhta HfO_2 ja CNT tipp-lainepikkustest. Esimene neeldumise tipp on seotud elektronide ergutumisega ületades HfO_2 valentstsooni ja juhtivustsooni vahe. Teine tipp on seotud molekulaarsete struktuuride defektidega ja pindmiste alamelektronkihtidega VHf ja Vo, mis ilmnevad HfO_2 valentstsooni ja juhtivustsooni vahele kui segada kokku HfO_2 ja CNT. Nende aktiveeritud alamelektronkihtide tõttu neelab HfO_2 rohkem pikema lainepikkusega ja madalama energiaga footoneid (~276nm) võrreldes puhta HfO_2 ja CNT'ga.

Lisades nanohübriidile CNT'd käitub see laengukandjana ning võimaldab rohkemate madalama energia footonite neeldumise, mida saab järeldada neeldumise intensiivuse erinevusest kahel tipplainepikkusel. Võrreldes puhta HfO_2 graafiku ja tipplainepikkustega intensiivsustega on nanohübriidi teine tipp kõrgemal. Tõstes CNT sisaldust 2% ja 5%-ni

kogukaalust, langes neeldumine tipplainepikkusel 2, mis on seotud alamelektronkihtidega, võrreldes neeldumisega tipplainepikkusel 1. mis on seotud elektronide ületamisega valentstsooni ja juhtivustsooni vahe. See on tõenäoliselt tingitud HfO2 nanoosakeste passiivsusest, kui HfO2 nanoosakeste pind küllastub CNT'ga.

Kõige efektiivsem valgusneeldumisega nanohübriidsegu oli madalaima CNT sisaldusega (1%), mis neelas kõige rohkem pikema lainepikkusega ja madalama energiaga footone, tipplainepikkusega ~276 nm. Kõigis proovides olid HfO_2 omadused domineerivamad võrreldes CNT omadega, 230 nm juures oleva tipu tõttu, mis on iseloomulik HfO_2'le.

Selles bakalaureusetöös esitatud tulemused näitavad monokliiniliste HfO_2-CNT nanokomposiitide suurt potentsiaali fotogalvaanilistes rakendustes, kuna neil on hea neeldumine UV-nähtavas vaguspektris. HfO_2-CNT nanohübriidkomposiiti võiks näiteks kasutada ühekihilise õhukese kilega päikesepatareina.

Vajalikud on täiendavad uuringud mõistmaks neeldumise käigus tekkivat mehhanismi ning põhjalikumaid uuringuid nanomaterjalide suhte muutmise mõju kohta. Samuti tuleks läbi viia fotovoolu genereerimise testimine nanohübriidile koosnevast monokliinilisest HfO_2'st ja CNT'st, kuna antud lõputöö keskendus ainult neeldumise lainepikkuste määramisele. Need lainepikkused võivad potentsiaalselt tekitada fotovoolu, kuid see ei ole kindlaks määratud. Selle materjali uurimise eeliseks on see, et HfO_2-põhiseid seadmeid juba toodetakse ja kasutatakse mikroelektroonikatööstuses, mis muudab nende integreerimise nanosüsteemidesse lihtsamaks. Juba välja töötatud tehniliste raamistike tõttu võib see kiirendada uute HfO_2-põhiste tehnoloogiate tootmist ja juurutamist.

APPENDIXES

LIHTLITSENTS

Lisa 1. Lihtlitsents lõputöö salvestamiseks ja üldsusele kättesaadavaks tegemiseks ning juhendajate kinnitus lõputöö kaitsmisele lubamise kohta

Mina Boris Ümarik

sünniaeg 27.09.1996 ,

1. annan Eesti Maaülikoolile tasuta loa (lihtlitsentsi) enda koostatud lõputöö

"A UV-visible Absorption Spectroscopic Analysis of Hafnium Dioxide and Carbon Nanotubes Based Nanohybrid Material for Solar Cell Applications

Päikeseelementide hübriidnanomaterjalide UV ja nähtava valguse analüüs - hafnium dioktsiid ja süsiniknanotorud"

mille juhendaja(d) on Protima Rauwel, Erwan Rauwel ja Yashita Khunger,

1.1. salvestamiseks säilitamise eesmärgil,
1.2. digiarhiivi DSpace lisamiseks ja
1.3. veebikeskkonnas üldsusele kättesaadavaks tegemiseks

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Tartu, 03.06.2021.

Juhendaja(te) kinnitus lõputöö kaitsmisele lubamise kohta

Luban lõputöö kaitsmisele.

Prof. Protima Rauwel, *PhD;*
Prof. Erwan Yann Rauwel *PhD*;
Ms. Yashita Khunger *M.Sc.*
/Allkirjastatud digitaalselt/ 03.06.2021